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Report on the Effects of High Energy Radiation on Cellulose and Other Polymeric Materials, A Literature Survey

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I. INTRODUCTION

A. Types of High Energy Radiations

The term, high energy radiation, as used in radiation chemistry applies to beams of accelerated particles and to high frequency electromagnetic radiations. Radiation effects are produced when energy is absorbed from the beams by the interactions of the radiations with the constituents of the irradiated system. High energy radiations may be supplied by particle accelerators, the best known of which is the X-ray machine. For the purposes of radiation chemistry an X-ray machine may be used to irradiate materials with cathode rays (accelerated electrons) or with the X-rays produced when the cathode rays interact with the target. The effect of x-rays on a photographic plate is an example of a chemical reaction with high energy radiation. Other types of particle accelerators are cyclotrons, betatrons, linear accelerators, Van der Graff machines, and synchrocyclotrons.

Atomic reactors produce neutrons which may be used to irradiate materials. Interaction of the neutrons with reactor materials yields beams of photons (or gamma rays), electrons and a variety of charged particles with higher masses. Materials under study may be irradiated simultaneously by the neutrons and their interaction products. Elements may be made radioactive by the absorption of the neutrons and in turn serve as sources of high energy

photons for radiation studies. An element extensively used for this purpose is Cobalt 60 which is formed by the capture of a neutron by a Cobalt 59 nucleus. In this isotope half of the atoms decay, within a period of 5.3 years, by the emission of gamma and beta rays to non-radioactive nickel. Thus a fairly constant and continuous source of high energy radiation is made available. The cobalt may be obtained in the form of thin wires which may be easily arrayed about the system under investigation.

Radium and its disintergration products have been used extensively for more than fifty years in research and in medicine. Their use in large quantities is prohibited by their scarcity but such radioactive materials as the cobalt isotope can now be substituted at less expense.

Photons and primary particles used in irradiation procedures are listed in Table I, together with nomenclature, origin and mode of production.

Table I. Types and Sources of High Energy Radiations

The terms x-ray and gamma rays are often used interchangably but the term gamma ray initially referred to photons of nuclear origin only. X-rays have both discrete energies and a continuous spectrum of energies but gamma ray energies are always discrete.

Table I. Types and Sources of High Energy Radiation.

Primary Particle	Nomenclature	Origin	Produced by
1. Photons	x-rays	Interaction of accelerated electrons with atomic shell electrons.	X-ray machines, betatrons, linear accelerators, etc.
	Gamma-rays (γ-rays)	Atomic nucleus	Radio active isotops, nuclear fission or disintegration.
2. Electrons	Cathode rays	Free electons in a metal or oxide.	X-ray machine.
	Beta-rays (B^--rays)	Nucleus Photon	Radioactive isotopes. Photon annihilation
	Delta-rays (δ-rays)	Atomic shell electrons.	Impinging radiation.
3. Positrons	Beta-rays (B^+-rays)	Nucleus Photon	Radioactive isotopes. Photon annihilation.
4. Protons	Hydrogen ion. (H^+)	Nucleus	Nuclear disintegration or fission.
5. Neutron	Nucleon (M^o)	Nucleus	Nuclear disintegration or fission.
6. Helium nucleus	Alpha particle (He^{++})	Nucleus Doubly ionized Helium.	Radioactive isotopes. Nuclear disintegration or fission, heavy particle accelerators.

Electrons, which are elementary negatively-charged particles, may be used to produce x-rays or to serve as a primary radiation. Electrons were known as cathode rays from their discovery as the cathode emission in early types of x-ray tubes. The term beta ray was first applied to electrons emitted by naturally occuring radioactive isotopes. The term delta ray is usually applied to high energy secondary electrons produced by ionization of an atom. Positrons have the same mass as an electron but with an equal and opposite charge. These particles are emitted by disintergrating nuclei or formed by annihilation of a high energy photon. An electron and a positron are always produced simultaneously when the quantum is annihilated.

Electrons and beta rays are often shown as e^- or e^+, B^- or B^+, and are also termed negative or positive beta rays and electrons. However, each is a single particle of mass 9.10×10^{-28} grams and a charge, positive or negative, of 4.80×10^{-10} electrostatic units.

Protons and neutrons are elementary nuclear particles. Protons have unit positive charge but neutrons are electrically neutral. The hydrogen atom contains but one proton in its nucleus and when ionized is a proton. Neutrons are produced only by nuclear disintegrations or by fission. The half-life of an emitted, uncaptured neutron is approximately fifteen minutes. Free neutrons disintegrate to form

a proton and a beta ray. The mass of the proton is 1.672 x 10^{-24} grams, of the neutron, 1.674 x 10^{-24} grams.

The term alpha particle was first applied to the helium nucleus emitted by naturally-occurring radioactive isotopes. Alpha particles have a positive charge of two and a mass equal to 6.60 x 10^{-24} grams. These particles may be produced by double ionization of helium.

Other nuclei may be used to produce beams of high energy radiation in particle accelerators but are usually employed for investigations of nuclear phenomena.

B. Dosage Determination

Photon and particle energies are customarily expressed in electron volts, ev. One ev is equal to 1.6 x 10^{-12} ergs and is defined as the kinetic energy acquired by an electron falling through a potential difference of one volt. The expressions, mega-electron volts or mev, and kilo-electron volts, kev, equal to 1.6 x 10^{-6} and 1.6 x 10^{-9} ergs, respectively, are most used because of the high energies of the radiations.

The roentgen, r, is most often used to measure the dose of radiation delivered to irradiated materials. The roentgen was originally defined as the quantity of x- or gamma- radiation which will produce in 0.001293 grams of air (one cubic centimeter) at S.T.P. one electrostatic unit, esu, of charge of either sign. Present usage denotes the

absorption of 83 or 93 ergs per gram of irradiated material. This quantity of energy is derived as follows:

1 esu $=(1/4.8 \times 10^{-10}) = 2.08 \times 10^{9}$ ion pair/r/cc

mean energy expended per ion pair in air = 32.5 ev

cc per gram of air = 1/0.001293 = 780

energy per gram of air = $780 \times (32.5 \times 1.6 \times 10^{-12}) \times 2.08 \times 10^{9} = 83$ ergs/r/gram

Other units have been proposed as more meaningful ones, for the r as originally defined covers only x- and gamma-radiation, from zero to three mev, and ionization in air. However, if used to denote the absorption of 83 or 93 ergs per gram of irradiated material the unit is still acceptable and widely used.

The activity of a radioactive material is measured in curies. One curie is equal to 3.700×10^{10} disintegrating atoms per second. If more than one radiation is emitted per disintegration, each must be considered in calculating dosage. The dose delivered to a gram of material by one curie of an isotope emitting one beta ray of 1 mev energy (average), all of which is absorbed in the volume considered is found to be

$1 \times 3.700 \times 10^{10} \times 1.6 \times 10^{-6} = 5.9 \times 10^{4}$ ergs per second. This is equivalent to $5.9 \times 10^{4} / 83 = 7.5 \times 10^{2}$ r/sec.

The disintegration of radioactive isotopes is a random process and the disintegration rate, usually denoted as λ, is the reciprocal of the time in which at least one atom may be expected to disintegrate. Calculations using a disintegration rate assume an extremely large number of radioactive atoms to be present. The half-life, T 1/2, or the time in which half of the radioactive atoms originally present, N_o, will have decayed is found as follows: Let N be the number of radioactive atoms present at a time t and $N = N_o e^{-\lambda t}$. Then when N/No = 1/2, and t = T1/2 and

$$\log 1/2 = -\lambda t$$
$$\log 1 - \log 2 = -\lambda t \quad \text{or } 0.693 = \lambda T\ 1/2 \text{ and}$$
$$T\ 1/2 = 0.693/\lambda$$

Thus a slower disentegration rate produces more uniform activity over long intervals of time though statistical variations will always be found.

C. Interaction of High Energy Radiations with Organic Materials.

Interactions which produce isotopes will not be discussed as it is not desired to produce radioactive products in the investigations proposed in this paper. An important generalization concerning the interactions of radiations with matter in radiation chemistry studies is that the wavelength of the radiation determines, in general,

whether the particular radiation will react with an electron, a nuclues, a whole atom or a whole molecule. The radiation will most probably react with the entity whose dimensions approximate its wavelength. Since particle or quantum energies are inversely proportional to their wavelength, it may be seen that the energies transferred to atoms and molecules are extremely low. Atoms (radius approximately 10^{-8}cm) present predominantly empty space to high energy radiations which average 10^{-10} to 10^{-12}cm. in wavelength. However the volume of the atom includes an electric field which interacts with the fields of the radiations. The most frequent interactions are with the loosely-bound atomic electrons, producing an accelerated electron which in turn produces ionizations.

Alpha rays and other heavy chaged particles are densely ionizing and their short path through matter, 20 to 40 microns in tissue, results in a densely ionized column. For particles with energies up to 10 mev, collisions are so frequent that the clusters formed by a single ionization unite to form a column of ionized particles.

The tracks of high energy electrons, or beta rays, consist of variously spaced clusters of ionized particles of varying sizes. High energy secondaries, delta rays, appear to fork off from the main track and form clusters at various intervals. The ionization density is approximately

1/1000 of that of an alpha particle. Electron interactions are of three types:(1) inelastic scattering, or ionization and x-ray production, proportional to the atomic number, Z; (2) elastic scattering or deflection by nuclear or electron fields with no energy loss and proportional to Z^2; (3) sharp deflections in which the electron radiates photons. The ratio of energy loss by radiation to that by ionization may be shown to be equal to ZE/820 where E is the energy of the impinging particle. in mev.

Photon reactions with matter are a function of the photon energy, and the atomic number and weight of the material. The three most important reactions are: (1) 10 to 60 ev, soft and medium x-ray region, photons are absorbed by the photoelectric effect wherein the total energy of the photon is absorbed and an electron is ejected from an inner shell with approximately all the photon energy, (2) 60 ev to 20 mev, photons are scattered by essentially free electrons, the scattered photon having a decreased frequency and the recoil electrons having a wide energy range; (3) from 20 to 100 mev., photons are attenuated principally by annihilation of the photon to create an electron and a positron and all the quantum energy is imparted approximately equally to the two particles. The interactions overlap but the most numerous are shown for each energy region.

Fast neutrons are slowed down in organic systems principally by collisions with hydrogen atoms. The atoms recoil as protons which produce dense ionization. Successive collisions usually yield thermal neutrons which are absorbed most probably by hydrogen to form deuterium and emit a gamma ray of energy equal to 2.2 mev. The mean life of a fast (greater than 10 ev) neutron is 10^{-4} seconds and the average velocity 2200 meters per second. Thermal neutrons make about one collision per centimeter of path and usually travel about 22 centimeters before absorption.

In the systems usually studied in radiation chemistry the effects of ionization and electronic excitation are the most important. In each of the primary absorption events described above, whether the event was an ionization or not, secondary effects are to produce ionizations or electron excitation. Secondary electons produced by heavy particles can have no more than twice the velocity of a heavy particle; a 1 mev particle produces a 2200 ev secondary. Any fraction of the energy of the incident electron may be transferred to a secondary electron.

The maximum energy of the primary radiation has no large effect on the distribution of secondary energies; the greatest number of secondaries have energies between the ionization energy and 100 to 200 ev. Secondary electrons dissipate their energies by transfer to external

atomic electrons, collision with energy transfer and by large angle deflection. The very low energy electron is finally absorbed to form a negative ion. A unit, called a "G" is often used to denote the number of events, ionizations or excitations, per 100 ev of energy absorbed.

Although the entire chemical effects of high energy radiations with matter have not been explored or explained, it is still believed that the results of radio-chemical reactions can be explained by a set of reaction steps similar to those of ordinary photochemical and thermal reactions. High energy radiation presents a large spectrum of energies for activation whereas photochemical reactions are activated by single energies or rather a very narrow range of energies.

Some laboratories capable of applying high energy radiation are listed in Table II.

Table II. Some Facilities for High Energy Irradiation of Materials for Radiation Chemistry Studies 1/

I. Fission Products and High Level Radiaisotopes--Gamma Rays

1. Phoenix Laboratory (Engineering Research Institute)
University of Michigan
Ann Arbor, Mich.

2. Food Technology Department
Massachusetts Institute of Technology
Cambridge, Mass.

3. Battelle Memorial Institute
Columbus, Ohio

4. Hanford Cooling Pit
Hanford Works, Richland, Washington.

5. Miscellaneous Medical Schools.

II. Particle Accelerators - High Energy Electrons and X-rays.

1. High Voltage Engineering Co.
Cambridge, Mass.

2. General Electric Laboratories
Schenectady, N.Y.

3. Food Technology Department
Massachusetts Institute of Technology
Cambridge, Mass.

4. National Bureau of Standards
Washington, D. C.

III. Reactors--Neutrons and Gamma Rays

1. AEC Facilities
(1) Brookhaven National Laboratory, Upton, N.Y.
(2) Oak Ridge National Laboratory, Oak Ridge, Tenn.

2. Universities
(1) North Carolina State College, Raleigh, NC.
(2) Penn State College (to be completed by mid 1955)

1/ This is not to be considered as a comprehensive listing.

II. GENERAL EFFECT OF HIGH ENERGY RADIATION ON LONG CHAIN POLYMERS.

The effects of high energy radiation have been studied on a variety of polymers. The data indicate two general effects: crosslinking of the polymer or rupture of the main valence polymer chain. In addition to these two main effects there are various minor effects such as the formation of unsaturated carbon-carbon linkages, and oxidation of the polymer when the irradiation is carried out in air.

According to the classification of Lawton, Bueche, and Balwit the following polymers have been shown to cross link under the influence of ionizing radiation:

Polyacrylic esters	GRS Rubber
Polystyrene	Butadiene-acrylonitrile copolymers
Polyesters	Neoprene W
Polyethylene	Neoprene GN
Chlorinated polyethylene	Polydimethylsiloxanes
Natural Rubber	Styrene-acrylonitrile copolymers

Within this series the polyethylene and polystyrene have probably been most extensively studied. The main source of high energy radiations used in these studies has been from atomic reactors (piles). The intensity is usually measured as the thermal neutrons per square centimeter, as the accompanying fast neutrons and gamma rays are assumed to be proportional to the slow neutrons. The total irradiation is then expressed as the slow neutrons per square centimeter (n/cm^2).

Generally, under low irradiation (less than 10^{17} slow neutrons/cm^2 with accompanying fast neutrons and gamma rays from a pile) this class of materials undergoes small increases in tensile and shear strength, while elongation is decreased considerably. The initial modulus, and hardness show some increase.

Under excessive irradiation (above 10^{18} n/cm^2) a drop in tenacity as well as elongation is observed with eventual disintegration of the materials. The development of a hazy appearance, increased moisture absorption, brittleness, and changes in color precede breakdown.

A wide variation is found in some physical properties at intermediate levels of irradiation. These are discussed individually.

Polyethylene and nylon show an increase in tensile and shear strength up to about 10^{18} n/cm^2, with only a small loss at 10^{19} n/cm^2. The elongation is reduced to a low value after 10^{17} n/cm^2 resulting in an increase in elastic modulus and hardness. The material becomes glass-like at room temperature. The characteristic hazy appearance is reduced which is in contrast to most plastics which become hazy upon irradiation. Irradiated polyethylene shows rubber-like elasticity and improved form stability above 100° C. where unirradiated polyethylene is viscous. X-Ray data, rate of cooling curves, temperature-density relations and viscosity and solubility studies

have been used to show the extent of cross linking and changes in crystallinity of irradiated polyethylene.

Natural rubber, neoprene, koroseal and polyesters also show an initial increase in strength with decrease in elongation but are disintegrated by about 10^{19} n/cm^2 irradiation.

Polystyrene had the greatest resistance to irradiation as 10^{19} n/cm^2 caused only minor changes in all physical properties.

While the mechanism of the cross linking process in these polymers is not completely understood, there is a large amount of evidence that the first step involved is an ionization or activation of part of the polymer chain due to interaction with an energetic secondary particle. This can result in the rupture of a carbon hydrogen bond, and by subsequent electron capture result in the formation of an active radical. Another alternative is the rupture of a carbon-carbon bond along the chain. While the latter is more feasible from a thermodynamical energetics consideration, ---the bond energy of C-C is approximately 80 kcal/mole whereas the C-H bond energy is about 98 kcal/mole --- the lack of mobility of the chain segment makes recombination more likely than in the case of the mobile H atom resulting from the C-H rupture. Experimentally, the ratio of the number of C-C ruptures of polyethylene to the

number of C-H ruptures has been found to be about 0.35; this has been established on samples over a wide range of initial molecular weights.

Charlesby found that irradiation of polyethylene by an ionization energy equivalent to 2.3×10^{21} ev. results in the crosslinking of 0.5 % of the carbon atoms present. In 1 gm. of polyethylene there are 2.15×10^{20} carbon atoms, so that the energy absorbed per carbon atoms is 11 ev, or 22 ev. per cross link formed. This is similiar to the energy of decomposition of butane by deuterium -- 10 ev.

Since the main effect of this radiation is to evolve H atoms and to form polymers from butane, the estimates of energy requirements in the vapor state compare directly with values for liquid and solid hydrocarbons .

It is important to realize that the effect of ionizing radiation does not depend on the state of aggregation of the polymer, the molecular weight of the polymer, nor the degree of crystallinity. Further the number of cross links effected is directly proportional to the amount of incident irradiation, and neglecting side effects, the time required for a given dosage is immaterial. Among those polymers which have been found to depolymerize, or degrade, under the influence of ionizing radiation are:

Polymethylmethacrylate
Polyvinyl chloride
Polyvinylidene chloride
Polytetrafluoroethylene
Polychlorotrifluoroethylene
Cellulose
Polyisobutylene

Methyl methacrylate, urea formaldehyde, vinylidine chloride polymers, casein, cellulose, cellulose acetate, cellulose nitrate, cellulose propionate, ethyl cellulose, and cellulose acetate buterate, all showed typical degradation, losing strength and elongation steadily with little change in the shape of the shape of the stress - strain curve upon irradiation. They became completely degraded at less than 10^{18} n/cm^2. Some also showed increases in weight and moisture absorption. All showed color changes.

Fluorethane and teflon, while showing changes similar to polyethylene at low irradiation, lost all strength at less than 10^{18} n/cm^2 .

Melamine formaldehyde, aniline formaldehyde, and phenolics had intermediate resistance, requiring 10^{19} n/cm^2 for complete loss in strength. Cellulosic fillers made little difference in resistance, while many plastics with asbestos fillers showed good resistance to irradiation.

It is difficult to predict the amount of energy required to disrupt a given type of polymer chain. Experiments indicate that 61 ev. of incident ionizing radiation are need per bond rupture in polymethylmethacrylate. Use of additives to the polymer such as allylthiourea, aniline, or di-m tolyl thiourea increase the energy requirements to 143, 153, and 227 ev., respectively. The same protective effect is obtained by copolymerizing a monomer

subject to degradation with a monomer inclined to cross-link. For example, polyisobutylene degrades, but a 20 % styrene addition in the form of a polyisobutylene-styrene copolymer protects the polymer so that degradation does not take place. It seems reasonable to assume that the crosslinking and degrading processes are competitive, and that in the case of the copolymer the effects are somewhat neutralized.

There is another mechanism by which this protective effect may operate. This is shown by the fact that aliphatic cyclic compounds are easily disrupted by high energy radiation, whereas the aromatic systems are not. This latter effect may be attributable to the ease with which conjugated systems absorb energy and are activated to higher quantum states; the activation energy may then be reradiated without bond rearrangement having occurred. The net effect of the conjugate system manifests itself then as an ability to absorb ionizing radiation without appreciable chemical change having occurred.

Both of these hypotheses may apply simultaneously since the presence of conjugated systems in a polymer not only increases the degradation energy requirements, but also aids in cross-linking. If, an activated molecule is the precurso to a chain linking event, then the conjugated system in its higher energy state would tend to facilitate the number of crosslinks formed, while at the same time acting as an inhibitor to chain rupture.

It is difficult to predict with certainty what the effect of ionizing radiation will be on any given type of polymer chain. However, there are some conclusions to be drawn from the data reported in the literature. It appears that unbranched linear polymers of the hydrocarbon type having a chain length of from seven to one thousand carbons can be crosslinked to form either gels or rigid polymers, depending on the initial chain length. With these polymers there appears to be little or no formation of unsaturation along the chain, and the energy requirements per crosslink are of the order of 22 ev.

On the other hand, polymers of the hydrocarbon type having neopentyl carbon atoms are degraded, and show the formation of appreciable unsaturation. It would appear reasonable to conclude that degradation - manifested as chain rupture - takes place in those structures which are able to form a more stable linkage within themselves than the activated form resulting from irradiation. Where the formation of such linkages is not possible, the activation energy is dissipated either by reradiation, as in the case of the conjugate systems, or by attack of the active radical on a neighboring group with the resulting formation of cross links.

This would explain the difference in behavior between polyethylene, containing only secondary carbon atoms, and polyisobutylene which contains neopentyl carbon atoms. The

mechanism postulated would consist of the initial activation of a carbon atom along the polymer chain, the dissipation of this activation energy either through energy transfer along the chain, reradiation of the energy, bond rupture and resulting skeletal rearrangement, or bond rupture and subsequent attack by the radical on neighboring polymer chains. The feasability of energy transfer along the skeletal chain is demonstrated by the protective effect given by additives to the polymer. The probability of activation of the polymer at points in contact with the additive is not great enough to cause the protective effect demonstrated; it must therefore be concluded that this protective effect is operative along a large length of the polymer chain, and this can only be explained by assuming that there is the feasibility of energy transfer along the chain. The possibility of reradiating the incident energy must be concluded from the ability of aromatic compounds to withstand the effect of large ionizing dosages; the reradiation of course may be in many forms, but presumably the larger part is in the form of heat. Bond ruptures due to ionizing radiation can be demonstra ted by the isolation of low molecular weight hydrocarbons in the case of degrading polymers, and in the isolation of hydrogen gas in the case of crosslinking polymers.

In a recent paper , Miller, Lawton, and Balwit have attempted to devine a general pattern for the behavior of solid polymers toward ionizing radiation. Their correlation of radiation effects and chemical structure applies only for vinyl polmers with main chains composed only of saturated C-C lerilrages. Even with this limitation a wide variety of polymers are covered by their generalization. They find that cross-linking occurs if the polymer contains at least one -hyrogen; i.e. if it has the structure $(-CH_2\ CH_2-)n$ or $(-CH_2\underset{R}{CH}-)n$.

Degradation will occur if the structural unit is $(-Ch_2\overset{CH_3}{\underset{R}{C}}-)n$.

While the postulates given would only apply to hydrocarbon type polymers, it would seem reasonable that the general principle could be extended to any type of polymer, providing sufficient knowledge is at hand about the relative energies of formation of the possible decomposition or crosslinked products. It would also require an extensive knowledge of the bonding energies present in a given type of polymer.

III. EFFECT OF HIGH ENERGY RADIATION ON CELLULOSIC MATERIALS

Although several other polymeric materials have been studied in some detail, there have been very few quantitative studies of the effect of high energy radiation on cellulose. A very interesting preliminary study of such effects has been made by Saeman and Millet, of the U. S. Forrest Products Laboratory, in cooperation with Lawton, of the General Electric Research Laboratory. High energy cathode rays as obtained from a modified 1-Mev X-ray unit were employed for the irradiation of wood, wood pulp, cotton linters, and glucose.

Unfortunately the radiation dosages applied to the cellulosic materials by Saeman; et.al., were rather large and the main effects noted were depolymerization of the molecular chains and decomposition of the carbohydrate constituents of the samples. With the cathode ray source employed a given ionizing dose could be accumulated at a rate of 143,000 roentgens (r) per second at a distance of 10 cm. from the tube window. Under the conditions of these irradiations the cotton linters sample experienced a temperature rise of about 40° C. during exposure to a radiation dose of 10^7 r. In those cases where a sample was to receive a total dose in excess of 10^7 r., the total dose was broken down into increments of 10^7 r. with a cooling period between irradiations.

The effect of irradiation with these high energy electrons on the degree of polymerization was determined from viscosity measurements in cupriethylenediamine. It was found that a dosage of 10^5 r. had small effect on the chain length of the cotton linters or wood pulp samples. At radiation dosage levels in excess of 10^6 r. a large decrease in the degree of polymerization was observed; the depolymerization effect increased with increasing radiation dosage up to 5×10^8 r. at which stage the cellulose was water soluble. In the dosage range between 10^6 and 10^8 r. the change of DP with dosage can be roughly approximated by a relation of the form:

$$\log \bar{DP} = -\alpha \log R + \log K$$

The viscosity data for the irradiated cotton linters and wood pulp indicate that depolymerization of both materials occured at the same rate. This coincidence in rate of depolymerization is to be contrasted with their behavior during chemical hydrolysis where the reaction rate for the crystalline portion of the wood pulp is approximately twice that for the same portion of the hydrolysis curve for the linters. This behavior suggests that the radiation induced depolymerization is independent of the extent or organization of the crystalline regions.

The original cellulose linters had an alpha-cellulose content of 97.7 %. Exposure to a radiation dosage of 10^7r. effected a 2% loss in apparent carbohydrate content. The

decomposition of carbohydrate increases with increasing irradiation dosage with a 44 % decomposition observed at a dosage level of 5×10^8r. At 10^7 and 10^8r. the carbohydrate loss in pure glucose was the same as the loss from cotton linters.

In addition to the reduction in degree of polymerization and carbohydrate decomposition, irradiation produced a large change in the susceptibility of the cellulose to hydrolytic attack by mineral acid. Samples of the irradiated materials were subjected to hydrolysis by 0.1N Sulfuric acid at 180° C. Extrapolation of the constant rate portion of the hydrolysis curve in the usual manner shows that increased radiation dosage produced an increase in the amount of easily hydrolyzed or "amorphous" cellulose. Irradiation not only causes an apparent decrease in crystallinity but also increases the hydrolysis rate for the crystalline or resistant portion of the irradiated cellulose. For example, the rate constant for the hydrolysis of the unirradiated cotton linters was 0.0058. After irradiation at a dosage of 10^7 r. the reaction constant was found to be 0.015 and after a dosage of 10^8 r. the reaction constant was 0.096.

Saeman, et. al. were interested in the saccharification of the irradiated cellulosic materials and were able to show that the over all sugar yield increased as a function of irradiation dosage. For example the linters showed an

increase in sugar yield from 23 % for the unirradiated control to 62.1% after exposure to 10^8 r. At radiation dosa es of greater than 5 x 10^8r., the overall yield of sugar drops off due to the increasing destruction of carbohydrate material. As regards the relation between DP and sugar yield, it was shown that the cellulose had to be depolymerized to an average chain length of about 200 glucose units before a significant increase in sugar yield was observed.

In the work of Saeman the two main effects noted as a consequence of radiation were depolymerization and decomposition. These two reactions occur simultaneously but at different rates. From the reduction in DP of the cotton linters affected by a radiation dosage of 10^8 r. it was possible to calculate that 1.02 x 10^{20} single depolymerization events must have occured per gram of linters. Since one gram of linters corresponds to 3.7 x 10^{21} anhydroglucose units, about one main chain fracture occured for each 36 glucose units.

The number of glucose units converted to non carbohydrate material by the same dosage is 5.2 x 10^{20} per gram of linters, or about one glucose unit in every seven is decomposed by a dosage of 10^8 r.

Saeman, et. al. point out that the depolymerization and decomposition reactions appear to occur at random both in the crystalline and amorphous areas and that the crystalline

regions remaining after irradiation are more subject to chemical reaction.

In working with the polymers polymethyl methacrylate and polyisobutylene Charlesby found that the change of viscosity with radiation is consistent with the assumption that degradation occurs by random fracture of the main valence chains and that the number of fractures is proportional to the radiation dosage. Applying these same considerations to the experimental work of Saeman, et.al., Charlesby has been able to give a theoretical amplification to their work on cellulose and to deduce simple relationships between dosage and depolymenization and decomposition.

Charlesby shows that the viscosity-average molecular weight of the irradiated sample (M_v') can be related to the applied dosage by the following equation:

$$M_v' = \left\{ p \left(\alpha + 2 \right) \right\}^{1/\alpha} \frac{m}{p} \left(R + R_o \right)$$

In this equation, m is the weight of a monomer unit, and p is the probability of main chain fracture occuring at a given monomer unit. R is the radiation dosage in units of 10^6 r. and R_o is defined as the "virtual" radiation needed to depolymerize a molecule of infinite molecular weight until the resultant has the same number-average molecular weight as the experimental polymer prior to irradiation. α is a constant which has a value between 0.5 and 1.0 depending upon the polymer system employed and is taken to be the same

as the exponent in the usual viscosity-molecular weight relation. The first term of the equation in brackets is the gamma function of $(\alpha+2)$ and gives the ratio between viscosity-average and number-average molecular weight for an exponential distribution of molecular lengths.

Further assuming that the correct form of the viscosity-molecular weight relation is:

$$[\eta] = K M_v^{\alpha}$$

then,

$$\log[\eta] = \log K + \log\{\Gamma(\alpha + 2)\} + \alpha \log \frac{m}{p} - \alpha \log (R + R_o)$$

If the above treatment is correct a plot of $\log[\eta]$ vs. $\log (R + R_o)$ should be a straight line of slope $-\alpha$. Charlesby uses the data of Saeman to check this relation and found that $\log[\eta]$ was linearily dependent upon $\log (R+R_o)$ with $\alpha = 0.71$ for cotton linters when R_o was 10^6 r. The value of K corresponding to $\alpha = 0.71$ was calculated to be 5.9×10^{-4}, and p was found to be 1.6×10^{-3}. According to this value of the probability, a dosage of 10^6 r. will fracture 0.16% of the bonds in the cellulose chains. On the basis of a 0.16% bond breakage per 10^6 r. there are 5.9×10^{18} bonds broken per gram of cellulose. This same radiation dosage liberates approximately 5.5×10^{19} electron volts per gram. Thus each main chain fracture requires only 9 e.v. This is appreciably lower than for isobutylene where 17 e.v. were required for each fracture.

Charlesby reiterates the conclusion given by Saeman that in radiation induced depolymerization the crystalline and amorphous regions are equally liable to main chain fracture. This conclusion is based on the linearity of the log [illegible] vs. log $(R+R_o)$ relation.

In the protection of cellulosic materials against thermal or biological attack it is usually necessary to modify only the amorphous portion of the cellulose. The crystalline or resistant portion has an inherent stability by virtue of its inaccesibility to the attacking agent. In any modification of cellulose designed for resistance to radiation, the protecting group must be distributed throughout the whole of the cellulose and not limited to substitution in the amorphous regions only.

Scocca and Brenner have discussed the role of moisture in the depolymerization of cellulose by x-rays. Samples of surgical cotton conditioned to different moisture contents were exposed to an X-radiation dosage of 10^6 r. Viscosity measurements on the irradiated samples showed that the oven dry samples were most severely depolymerized while those containing 6-14% moisture were much less severely degraded.

Lawton, Bellamy, Hungate, Bryant, and Hall have studied the effect of high energy electrons on bass wood. Irradiation of basswood altered its structure in such a way that some of the insoluble carbohydrate became available to rumen bacteria.

The digestability of the wood was little affected by radiation dosages of 6.5×10^6 r. or less. Between 6.5×10^6 and 1.0×10^8 r. increased dosage resulted in increased formentability. Maximum formentability was obtained at a dosage level of 10^8 r. At this point of maximum digestability the wood became friable and hygroscopic. At radiation dosages greater than 10^8 r. the carbohydrate fraction was converted to a form less readily usable by rumen bacteria.

Winogradoff has made a brief study of the effect of X-radiation on the tensile strength and other properties of cellulose acetate filaments and films. Samples of cellulose acetate yarns were exposed to x-radiation eminating from a copper target tube operated at 50 Kvp for periods up to 190 hours. The tensile strength was found to decrease exponentially with exposure time. The tensile strength decreased to less than 50% in 120 hours of exposure. Each tensile failure occured within the irradiated area of the yarn and showed very brittle fracture.

X-ray diffraction patterns obtained on irradiated samples of the cellulose acetate showed that a progressive decrystallization was effected by increased radiation dosage. Winogradoff was able to show further that a gas was evolved during the irradiation of cellulose acetate.

In summarizing the effects of high energy radiation on cellulose, it must be noted that the main chemical effects discussed in the literature are those of depolymerization,

decomposition, and decrystallization. Thus at the dosage levels previously studied the effects of radiation on cellulose are to a large extent detrimental. It will be necessary to study lower dosage levels to determine if there are any beneficial effects of radiation on the textile properties of cellulosic materials. Some of the possibilities of improving cotton cellulose by low level irradiation are suggested in a later section.

IV. APPLICATION OF HIGH ENERGY RADIATION IN CELLULOSE MODIFICATION AND TREATMENT .

As was pointed out in the last section the main effects of radiation on cellulose itself are depolymerization and decomposition. Thus the application of high energy radiation would appear to have no place in the treatment and modification of cellulose. However, in the modification of cotton with the view to imparting or improving certain characteristics, it is often necessary to use other polymeric materials in conjunction with the cellulose. For example, polymethyl siloxanes are applied as water and soil resistant finishes. Impregnation with acrylonitrile butadiene copolymers and other emulsion latices have been employed for the improvement of abrasion resistance. In the application of crease proofing resins, the monomer or precondensates are deposited in the fiber followed by in situ polymerization to give a block polymer.

It is in such cases where a secondary polymer or monomer is used in conjunction with the cellulose that the possible usefulness of high energy radiation becomes apparent. Polymerization of applied monomers may be induced by radiation. These radiation induced polymerizations have certain advantages over chemically catalyzed polymerizations which make them specially attractive in textile finishing work. The polymerization reaction may be carried out at a much

lower temperature and the molecular weight of the resulting polymer is directly proportional to the temperature, as compared to chemically catalyzed reactions when the resulting molecular weight is inversely proportional to temperature. These advantages follow from the fact that in radiation induced polymerization the active centers are produced by a temperature independent process.

A second major possibility lies in the cross linking of preformed polymers deposited on the cellulose surface by impregnation from solution or emulsion. Although the polymer network so obtained would not be chemically bonded to the cellulose, an improvement in launderability and heat stability should be accomplished in transforming the initially deposited linear polymer into a cross-linked network. The latter effect is feasible because of the tremendous amounts of localized energy which are available for bond rupture and bond rearrangements due to secondary particle collisions. The low temperature in situ polymerization of vinyl and acrylic type monomers in cellulose should be considered. It has been found possible to polymerize these monomers at a temperature of 30° C under the influence of a radiation dosage of 10^6 r. with a conversion better than 50% based on monomer. Acrylamide can be polymerized at 0° C with a dosage of 2×10^6 r. in the solid state. The same dosage will polymerize tetraethylene glycol dimethacrylate (Tegma) at temperatures of -55° C.; this latter

compound shows the odd property of storing free radicals. For example, if TEGMA is cooled below -55° C. and irradiated at this temperature, no polymerization takes place. If the compound is then heated above this temperature, the polymerization begins, even if the irradiated monomer has been stored at dry ice temperatures for several days after irradiation.

Cross linking of preformed polymers should be of interest in improving the laundry resistance of water repellent finishes. A reaction of interest would be the formation of cross-linked polydimethylsiloxanes in situ with ionizing radiation.

There is a possibility that cotton impregnated with natural or GRS rubber could be given improved adhesive properties by cross-linking the rubber with ionizing radiation. The crosslinking of the rubber should improve the adhesion between the cellulose and polymer, and the latter would facilitate adhesion to other hydrocarbon type structures.

One of the new fields for application of ionizing radiation is in the radiation induced polymerization of such compounds as perfluoropropylene, perfluorobutadiene, and perfluore acrylonitrile; these compounds can not be polymerized by ordinary chemical catalyst. It may be possible therefore to polymerize those compounds after impregnation of the monomer into cotton and thus produce a tightly bound fluorine containing polymer in the fiber. In the liquid state a dosage of 10^6 r. has been found to convert from 0.10 to 0.24% of these monomers into polymeric form.

There seems to be little likelyhood of directly cross linking cellulose through the use of ionizing radiation. Such cross links may be feasible in cellulose derivatives containing vinyl groups. For example, if cellulose acrylate were exposed to ionizing radiation there is the possibility of forming vinyl polymers between the cellulose through the acrylate double bond.

It must be emphasized that in all of these suggested applications there will be a competition between the desired reaction and the degradation reaction of cellulose chains and glucose rings. The feasibility of each type of reaction would have to be determined experimentally to find a workable dosage level which would produce the desired polymerization or cross linking reaction without causing prohibitive degradation. In some cases it may be necessary to work with chemically modified cellulose containing aromatic resonant substituents in order to afford the cellulose some protective effect. An example of this would be the benzyl ether derivative of cellulose or even the cellulose benzoate.

V. USE OF RADIOACTIVITY FOR CONTROL OF STATIC ELECTRICITY IN TEXTILE PROCESSING.

Static electric charges are generated on textile fiber as they rub against each other or against the machinery during processing. If the fibers are sufficiently conducting, the

charges will be immediately neutralized, but as many fibers are good insulators the charges remain and cause undesirable attractive and repulsive forces which interfers with processing in many ways.

Raw cotton and wool are fair conductors at high humidities so the static electric problem was not severe until the development of synthetic fibers and chemically treated cottons. These are often less hydroscopic and lack natural lubricants, both factors contributing to development of a static charge. Competition for quality with increased speed of production makes the problem acute.

The current required to dissipate the charge developed in various operations varies from about 0.003 microampere in weaving and 0.07 microampere in carding, to as much as 5 microamperes in warping operations.

Static may be controlled in a number of ways depending upon the material and processing stage. All metal parts of machinery should be well grounded, and the material itself may be partially grounded by passing it close to sharp points on grounded bars. The use of high humidity is advantageous where the material is hydroscopic and its strength is not adversely affected by absorbed moisture. Very high humidity corrodes machinery. Cationic and anionic conducting chemicals and lubricants are also effective, especially where friction must also be controlled but are expensive if used in sufficient

quantity and may also have to be removed before further processing. Sources of high voltage discharges have been developed to relieve static charges and may be the only feasable method where currents of greater than about 2 microamperes are involved, as in warping operations.

Ions created in the material and the surrounding air by high energy radiations from radioactive material are effective in allowing conduction either via the air or the material to grounded parts of the machinery. Little progress in this direction has been made heretofore because of the scarcity of economically available radioactive materials. There are principally three types of particles from radioactive material useful as ionizing agents.

Gamma rays are extremely dangerous in amounts sufficient to produce the required ionizations, as they are very penetrating and heavy metal shielding is required to control them. Alpha rays are the strongest ionizing agent and the safest because of their short range and low penetrating power allowing easy shielding and causing only surface burns when carelessly handled. They are especially useful where the material can be made to pass very close to a coating of the material. Radioactive Polonium is a good source of alpha rays but is expensive and has a short half-life. Radium sources emit alpha as well as Beta and gamma rays but are dangerous, principally because of the gamma rays.

Beta rays are intermediate in safety requiring some shielding and can be used where the dissipation current required is not too high. They could possibly be used in carding effectively if strong enough sources can be obtained cheaply. Thallium 204 is a cheap and safe source of beta rays but is not available in sufficient strength for carding operations. It also has a short half life (2.7 years). Strontium 90, with a 22 year half life emits beta rays and should be available from nuclear reactors (piles) in quantity.

The Shirley Institute has used Thallium 204 as an oxide coating on brass to eliminate "fog marking" of material during weaving. The electrostatic charge left on the material after the loom has stopped collects dust, etc., giving the exposed material a grey color. The beta ray source is suspended over the loom during shut-down periods to dissipate static charges. These sources are safe when properly handled.

VI. SUGGESTED RESEARCH ON THE INTERACTION OF COTTON CELLULOSE AND HIGH ENERGY RADIATION

Two points are evident in considering possible future work on the application of high energy radiation in cellulose research. First, the effects of radiation on cellulose in the form of textile products has not been studied at all, and, second, those studies of cellulosic materials which have been made were sacrificial in nature in that the desired end was the destruction of the cellulose. For example, in the one case

where cotton linters were irradiated the starting material was a commercial sheet already largely degraded (DP = 900) during chemical purification. The linters were then exposed to high level radiation dosages with the intent of improving the sugar yield by saccharification of this irradiated cellulosic material.

A first and fundamental study is desirable on the effects of radiation on native cotton cellulose in textile form --- fibers, yarns, fabrics, etc. In such a study the exposure level should be considerably lower than that previously employed since it is known that the radiation threshold for depolymerization and decomposition of cellulose is about 10^6 r. The range of radiation dosage from about 10^3 r. up to the destructive threshold should be surveyed to determine if there are beneficial effects of radiation on textile properties. A partial list of qualities that should be evaluated as a function of dosage are given below:

1. Tensile properties--strength, tenacity, elongation, elastic modulus, elastic properties, etc.

2. Fine structural properties--crystallinity, crystalline orientation, density, swellability, moisture absorption, etc.

3. Molecular Properties--degree of polymerization, configurational study of resulting glucosides, etc.

4. Chemical Properties--reactivity and accesibility, rot resistance, heat resistance, etc.

The moisture content of the cotton undergoing irradiation can be expected to modify the course of the induced reactions and would require study. The nature of the surrounding atmosphere during irradiation can also be expected to play a part in the nature of the effects produced and would require control.

Although a detailed study of the effects of radiation on native cotton would be a large undertaking, secondary studies should also be considered for some of the more important modified cottons---mercerized, acetylated, cyanoethylated, decrystallized, etc. It should be noted that with the exception of the actual irradiation work all of the characterization tests are common to cellulose research and would require no large outlay for equipment or personnel not presently available.

Research on the use of ionizing radiation in the modification of cotton can be divided into two broad classes. The first would include the study of irradiation effects on cotton impregnated with various materials. Among these would be uncured elastomers, preformed polymers or copolymers, and reactive monomers which could be polymerized in situ. The second broad grouping would include cellulose derivatives which might be induced to cross link because of functional groups which they contain; an example of this would be the tetraethylene glycol methacrylate ether of cellulose. The parent compound containing the two terminal methacrylate groups

is easily polymerized at 0° C. under the influence of high energy radiation.

Another interesting topic for research would include the effect of radiation on the known chemical reactions of cellulose. For example, formaldehyde will react with cellulose in acidic media. It would be of interest to radiate cellulose in an atmosphere of formaldehyde vapor to determine if cross linking can be obtained in this manner.

The use of radioactive isotopes in mechanical processing will depend upon the economic availability of isotopes giving alpha and beta radiations in sufficient strength. A study should be made of the probable cost of various radioactive isotopes having the desired properties. It has already been suggested that Strontium 90 should be available from nuclear reactors in quantity. If it appears that desirable isotopes are available economically then a study of methods of using them to relieve static electric problems would be in order.

In view of the bactericidal properties of high energy radiations, the feasibility of utilizing this effect for sterilization of cotton products has been considered. For example, the cotton bandage developed at this Laboratory might be exposed to high energy radiation rather than to heat in a sterilization process. One hundred percent reduction of viable, spore-forming bacteria, containing originally an abundant number of spores, has been obtained with a dose of 2.04 x 10^6 r.

The bacteria were irradiated while suspended in a saline and gelatine solution. Other investigators have found the lethal dose to be of the same order of magnitude. It should be bourne in mind that the percent kills of microorganisms reported are very dependent on the extent of sampling. However, reported lethal doses are usually those in excess of doses required for 99.9 and 99.99 percent kill. For any particular strain of organisms, the lethal dose is a function of the suspending medium, the surrounding atmosphere, and the density of ionization produced by the radiation. Since the degradation of cotton cellulose begins at doses of approximately 10^6 r., further study is indicated before this technique of sterilization can be accepted as completely feasible.

MG/ 3/31/55

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